

Surface charge pattern: Impact on vibrational spectroscopy and physics of charged interfaces

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Surface-specific vibrational spectroscopies revolutionized the study of charged interfaces, by sensitively probing water's response in the electric double layer (EDL) and correlating it with surface charge via models like Gouy-Chapman-Stern. The assumed one-to-one relationship between water's spectroscopic response and surface charge has been widely accepted without question. We hereby propose a theoretical experiment to evaluate this assumption. Interestingly, our findings reveal a non-one-to-one relationship between surface charge and spectroscopic response, exhibiting a fascinating dependence on surface topology.

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I. INTRODUCTION

What is the protonation state of an oxide surface in contact with liquid water? What is the point of zero charge of an electrode-electrolyte interface? How do ions (and water) arrange and screen the electric field within the electric double layer (EDL)? Despite more than a century of intensive research, these fundamental questions in interface science remain challenging to address, both in theory and experiment [1–10]. In the last decades, surface specific spectroscopies, such as vibrational sum frequency generation (vSFG) and second harmonic generation (SHG), have opened a possibility of gaining insights by sensitively probing the response of water within the EDL [1–3,10–31]. This response is often used to deduce the surface charge (σ), via a commonly assumed one-to-one correspondence based on the Gouy-Chapman-Stern (GCS) model and its derivations [13–15,18,21,25,26,31].

SFG and SHG experiments probe the second-order susceptibility $\chi^{(2)}$, which is interface-specific since $\chi^{(2)} \neq 0$ only for noncentrosymmetric media, e.g., aqueous interfaces, while $\chi^{(2)} = 0$ in the centrosymmetric bulk [32–34]. The $\chi^{(2)}$ response from a charged interface is given by the sum of two

contributions respectively arising from the topmost binding interfacial layer (BIL, where the molecular organization and H-bond network substantially differ from bulk aqueous solutions because of the direct contact with the surface and ions adsorption), and from the subsequent diffuse layer (DL, composed of bulk-like water oriented by the surface electric field and by dissolved mobile ions) [1–3,10,14,16,18,25,27–29,35],

$$\chi^{(2)}(\omega) = \chi_{\text{BIL}}^{(2)}(\omega) + \chi_{\text{DL}}^{(2)}(\omega). \quad (1)$$

$\chi_{\text{DL}}^{(2)}(\omega)$ contains the response of water within the EDL. Nowadays, several approaches have been devised to extract $\chi_{\text{DL}}^{(2)}(\omega)$ from the measured $\chi^{(2)}(\omega)$ [1–3,14,16,25,35], and most recently techniques that are specifically sensitive to $\chi_{\text{DL}}^{(2)}(\omega)$, such as phase resolved SHG, have been developed [18,31]. As remarked in many studies, $\chi_{\text{DL}}^{(2)}(\omega)$ can be expressed as

$$\chi_{\text{DL}}^{(2)}(\omega) = \chi_{\text{Bulk}}^{(3)}(\omega) \int_{z_a}^{\infty} dz \cdot E_{\text{DC}}(z) e^{i\Delta k_z z}, \quad (2)$$

where $E_{\text{DC}}(z)$ is the electric field profile along the z direction perpendicular to the surface and Δk_z is a phase factor that takes into account interferences between the emitted light at different depths from the surface [14,15,21,24,25,35]. The integral runs across the EDL region, with z_a being the boundary between BIL and DL. $\chi_{\text{Bulk}}^{(3)}(\omega)$ is the bulk water third-order susceptibility [14,25]. The surface charge σ is usually determined by using GCS to approximate the $E_{\text{DC}}(z)$ dependence on z . The prerequisite of this model is that, at fixed electrolyte composition, the same σ must always result in the same $\chi_{\text{DL}}^{(2)}(\omega)$.

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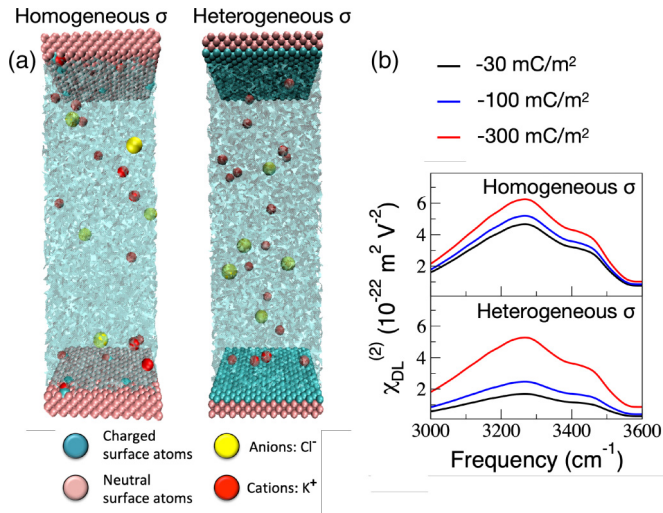


FIG. 1. Theoretical experiment challenging the commonly assumed one-to-one correspondence between $\chi_{\text{DL}}^{(2)}(\omega)$ and σ . (a) MD snapshots illustrating the model interfaces with homogeneous and heterogeneous σ patterns (for $\sigma = -100 \text{ mC/m}^2$ as an example). (b) $\text{Im}\chi_{\text{DL}}^{(2)}(\omega)$ spectra computed from six MD simulations. The intensity is markedly different for heterogeneous vs homogeneous surface charge distributions: σ cannot be deduced from $\chi_{\text{DL}}^{(2)}(\omega)$ without knowing the surface pattern.

Since the seminal work of Eiseenthal and coworkers [13], this approach has been widely employed to perform SHG and SFG spectroscopic titration for oxide surfaces in contact with aqueous solutions of varying pH [2,13,16,36–39], to study the way electrolyte solutions screen the surface field [1–3,14,17,27,28,31,35,40–42], to determine the charge state of the surface and the solution response in electrochemistry [10–12,30,43–46], and to probe charge separation and recombination during interfacial chemical reactions [47–49], to cite a few. Each of these studies substantially advanced our understanding of the complex chemophysical properties of charged aqueous interfaces. However, despite being at the heart of this emerging research field, the assumption that one and only one $\chi_{\text{DL}}^{(2)}(\omega)$ corresponds to one given σ value (for fixed electrolyte composition) has never been assessed. One reason is that such an assumption is implicitly encoded in our textbook understanding of the EDL response to the electric field.

We test this hypothesis with a theoretical experiment, by means of classical molecular dynamics (MD) of the minimal required complexity. Our focus is on the $\chi_{\text{DL}}^{(2)}(\omega)$ term only, since, as discussed above, it is the one used in state-of-the-art approaches to deduce surface potential and surface charge from SFG/SHG measurements. The $\chi_{\text{DL}}^{(2)}(\omega)$ is well recognized to be surface specific. Therefore, the theoretical experiment outlined hereafter does not provide new insights on $\chi_{\text{DL}}^{(2)}(\omega)$.

II. METHODS

We used the LAMMPS [50] code to simulate a 35 mM NaCl aqueous solution between identically charged walls [Fig. 1(a)]. To keep the model as simple as possible, the

walls were constructed to represent a generic weakly interacting surface, with interaction parameters introduced by Huang *et al.* [51,52]. The ion concentration was kept intentionally low to ensure that we remained within the range of validity of GCS, while being high enough to avoid unwanted interference effects in the $\chi^{(2)}(\omega)$ [15].

The water+NaCl system is described using the force field developed by Kann and Skinner [53], with TIP4P/2005 water and rescaled (by 0.85) ion charges. Charge rescaling effectively describes ion polarizability [53]. Lorentz-Berthelot mixing rules are adopted for wall-electrolyte interactions. We systematically considered $[\text{NaCl}] = 35 \text{ mM}$ and added the appropriate number of sodium counterions to generate neutral simulation boxes, containing a liquid phase of 11 465 water molecules (held rigid using the SHAKE algorithm). To impose a pressure of 1 atm, the top wall was used as a piston until an equilibrium height was reached, yielding box dimensions in the xy plane of 48.2 Å and a vertical z dimension of 267 Å. Subsequent equilibration and production runs were 32 ns each (NVT ensemble, $T = 298 \text{ K}$, Nosé-Hoover thermostat [54]). The surface charge was implemented in two ways: (i) a homogeneous distribution across all topmost wall atoms; (ii) a heterogeneously distributed surface charge, randomly assigned to only some of the topmost atoms. A total of six model systems were considered, with $\sigma = -30, -100, -300 \text{ mC/m}^2$, covering the typical surface charge densities for silica/water interfaces in the 2–14 pH range [4,16,27,41]. Indeed, most SFG/SHG titration studies have been performed on silica/water interfaces [2,13,16,36–38], where SiOH terminations and therefore surface charge patterns can be more or less heterogeneous depending on the way the surface is pretreated [55–57]. These studies, such as those by Gibbs *et al.* [3,37,38] and many others [2], have yielded some of the most intriguing yet controversial results in the field of interface spectroscopy, revealing a still-unexplained dependence of the spectroscopic response on surface preparation methods.

Theoretical SFG spectra were computed following the procedure of Ref. [58]. In short, $\chi_{\text{DL}}^{(2)}(\omega)$ was obtained by the Fourier transform of the dipole (μ)-polarizability (α) correlation function [59], considering all the cross-correlation terms between the N_{DL} water molecules located in the DL layer and all the N_{W} water molecules of the simulated system,

$$\begin{aligned} \chi_{\text{DL}}^{(2)}(\omega) &= \frac{i\omega}{k_{\text{B}}T} \sum_{i=1}^{N_{\text{DL}}} \left(\sum_{j=1}^{N_{\text{W}}} \int_0^\infty dt e^{i\omega t} \langle \alpha_{xx}^j(t) \mu_z^i(0) \rangle \right) \\ &= \sum_{i=1}^{N_{\text{DL}}} \beta_{\text{DL}}^i(\omega), \end{aligned} \quad (3)$$

where $\beta_{\text{DL}}^i(\omega) = \frac{i\omega}{k_{\text{B}}T} \sum_{j=1}^{N_{\text{W}}} \int_0^\infty dt \exp(i\omega t) \langle \alpha_{xx}^j(t) \mu_z^i(0) \rangle$ is the contribution of the i th DL-water molecule. The SFG activity of DL-water is dominated by the dipole orientation of the water molecules [14,24,25], which hence leads to $\chi_{\text{DL}}^{(2)}(\omega)$ being calculated via the following equation [58]:

$$\chi_{\text{DL}}^{(2)}(\omega) = \sum_{i=1}^{N_{\text{DL}}} \frac{\beta_{\text{DL}}^i(\omega)}{\cos \theta_i} \cdot \cos \theta_i, \quad (4)$$

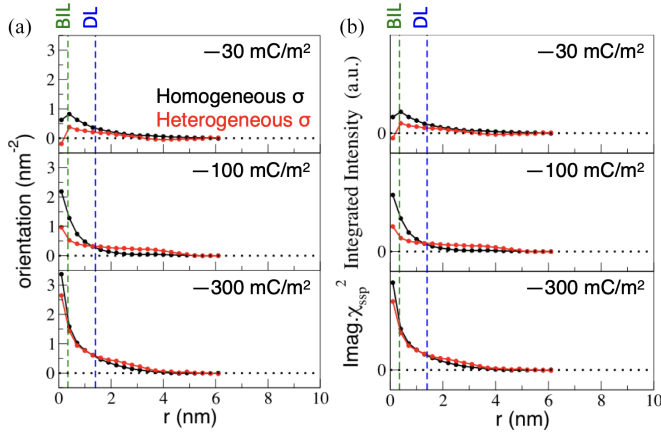


FIG. 2. Surface pattern influences the electrolyte response in the DL (diffuse layer). (a) Water orientation profile ($\sum_{i=1}^{N_w} \cos \theta_i$ normalized by surface area, see Eq. (4) in the method section) along r —the vertical distance from the surface. (b) Corresponding r -profiles for $\text{Im} \chi_{\text{DL}}^{(2)}(\omega)$ intensity (integrated over $3000 - 3600 \text{ cm}^{-1}$), as computed from $\sum_{i=1}^{N_w} \cos \theta_i$ with Eq. (4) (Method section). The vertical green dashed line marks the boundary between BIL and DL regions. The blue dashed line marks a plane located 1 nm within the DL.

where the orientational term (with θ_i being the angle formed between the dipole of the i th water molecule and the normal to the surface) is directly obtained from the MD simulations, while $\frac{\beta_{\text{DL}}^{(2)}(\omega)}{\cos \theta_i}$ has been parameterized in Ref. [58]. Figure 1(b) reports the computed theoretical SFG $\text{Im} \chi_{\text{DL}}^{(2)}(\omega)$ spectra for all systems.

III. RESULTS

Based on the current state of knowledge, we expect the $\text{Im} \chi_{\text{DL}}^{(2)}(\omega)$ spectrum to be identical for model interfaces with the same surface charge σ , regardless of whether the charge distribution is heterogeneous or homogeneous. However, this is not what we observe in Fig. 1(b).

All $\text{Im} \chi_{\text{DL}}^{(2)}(\omega)$ spectra exhibit a two-band structure, with maxima at ~ 3200 and 3400 cm^{-1} [14,60]. This is expected from many previous experimental and theoretical studies: the shape of the $\chi_{\text{DL}}^{(2)}(\omega)$ spectrum originates from the $\chi^{(3)}(\omega)$ spectrum of bulk water Eq. (2); therefore, it is similarly observed at different charged interfaces (unless molar ions concentrations are introduced into the liquid or temperature is varied) [14,15,21,24,25,35]. Strikingly, the intensity is higher (by up to three times) for homogeneously charged surfaces than for their heterogeneous counterparts. This result is consistent with a previous study from Dewan *et al.*, where the way the surface is charged was shown to influence ion adsorption, hence the screening within the EDL region [61]. The difference in our computed $\text{Im} \chi_{\text{DL}}^{(2)}(\omega)$ spectra is most marked for the lowest σ , and slowly decreases—but persists—with increasing charging. The molecular origin of this effect lies in the sensitivity of the field-induced water alignment to the surface charge patterning, as shown in Fig. 2 (left) by means of water orientation profiles. These are particularly informative since the net water orientation in the DL region is directly

proportional to the intensity of $\chi_{\text{DL}}^{(2)}$ [Eq. (4)], as shown in Fig. 2 (right).

All orientation profiles show the expected decay after the boundary between BIL and DL (green-dashed line); the magnitude, however, is different from case to case and follows the trend observed in the topmost interfacial BIL layer. The orientational response of BIL water (before the green dashed line) substantially differs depending on the way the surface is charged: BIL (as well as the subsequent DL) water is systematically more efficiently aligned by the homogeneous rather than the heterogeneous surface charge distributions (black vs red in the plot). This is not surprising since many recent studies, both theoretical and experimental, have demonstrated how sensitive the arrangement of hydration water is to the way the polar/charged groups are distributed over the surface [62–70]. This is because the water response does not depend on single water-surface interactions, but on the collective rearrangement of the water H-bond network in response to the local distribution of polar groups at the surface [62,65–68,70]. In particular, studies on the wetting of patterned surfaces have shown that the surface is most wet, and accordingly, the water H-bond network is most perturbed, when the polar groups are dispersed as homogeneously as possible over the surface, while the effect is minimized when the polar groups are clustered over a few small surface areas [66]. The same reasoning can be applied here to explain why BIL and DL water molecules are best aligned by the homogeneous charge distributions.

These changes in the H-bond network are quantitatively investigated in Fig. 3. They are not visible in the water density profiles of Fig. 3(a), where the first density peak identifies the BIL, while the subsequent minimum marks the BIL/DL boundary accordingly to the well-tested definition of Refs. [2,25–27,41,56,71]. Not surprisingly, water density is a poor descriptor of surface wetting [62,72–74]. However, the effect of surface charge distribution becomes evident when analyzing the H-bond network formed by BIL water molecules. Figure 3(b) reports the average number of H-bonds (HB) formed by a BIL-water molecule with other BIL-water molecules, i.e., intralayer (red), and with water molecules in the adjacent DL region (inter, blue). The Luzard-Chandler [75] distance+angle criterion is used to define HBs (we checked that the trends observed in the figure are conserved by varying the distance and angle cutoffs). The statistical error (standard deviation after dividing each simulation into 10 blocks) is < 0.1 HBs/molecule. As a reference, values of 2.0 intra-HBs and 1.0 inter-HBs are computed for the uncharged surface, where BIL-water adopts a preferential horizontal orientation within the H-bond network, maximizing intra-BIL HBs as typical of weakly interacting surfaces [28,71,76]. Surface charging is expected to perturb this horizontal ordering, by aligning water along the surface field, hence converting intra- into inter-HBs. Such perturbation is clearly observed for the homogeneously distributed surface charge, where the population of inter-HBs rapidly overcomes that of intra-HBs with increasing σ . In stark contrast, intra-HBs remain dominant for the heterogeneously charged surface until the largest $\sigma = -300 \text{ mC/m}^2$, resulting in a less efficient response in alignment of the interfacial water along the surface field.

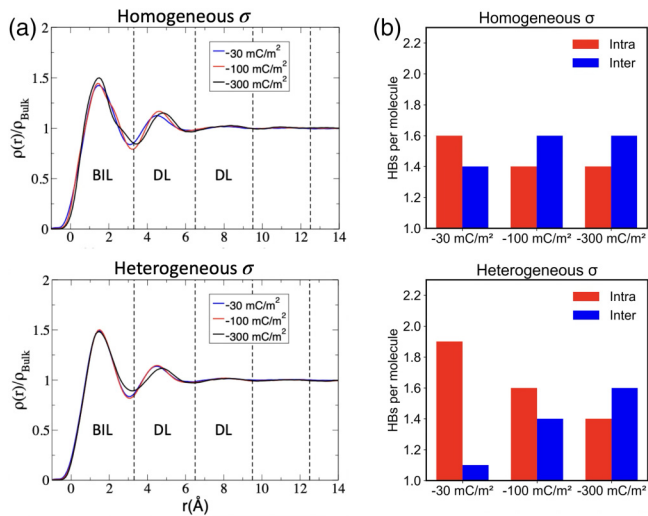


FIG. 3. The effect of surface charge distribution on interfacial water structure. (a) Density profiles of water at homogeneously (upper panel) vs heterogeneously (lower panel) charged surfaces. Surface charge distribution has little influence on the density profiles of water, which is known to be a poor descriptor for surface wetting. (b) Average number of H-bonds/water formed among water molecules in the BIL (Intra, red) and between BIL-water and the adjacent DL region (Inter, blue) at homogeneously/heterogeneously charged surfaces. The ratio of intra/inter H-bonds indicates the horizontal/vertical ordering of the interfacial H-bond network. For uncharged weakly interacting surfaces, 2.0 intra-HBs and 1.0 inter-HBs were computed for reference. Homogeneous surface charges restructure more efficiently the interfacial HB-network than heterogeneously distributed charges, better promoting vertical water alignment with the surface field.

IV. CONCLUSIONS

In conclusion, the result of our theoretical experiment challenges the commonly assumed one-to-one correspondence between the surface charge and the electrolyte response to the electric field at the interface, as measured by $\chi_{\text{DL}}^{(2)}(\omega)$: indeed, we showed that the same σ value can result in significantly different $\chi_{\text{DL}}^{(2)}(\omega)$ responses depending on the specific distribution of charge across the surface. This insight may help explain the unresolved findings from the past 30 years

of SFG/SHG titration studies on silica/water interfaces, where variations in surface charge patterning (i.e., the distribution of SiOH terminations) likely arose because of differences in surface preparation across studies [3,37,38,55–57]. Our findings indicate that such charge patterning results in significantly different SFG/SHG intensities, as a function of pH.

More generally, our results also demonstrate that the electrolyte screening within the EDL is a three-dimensional (3D) problem, sensitive to the lateral charge distribution over the surface, together with the specific properties of the interfacial water H-bond network. This calls for further developments of EDL theories, beyond commonly adopted 1D models (e.g., GCS and its derivatives), where surface topology and molecular interactions should be explicitly included, in line with recent insights from MD simulation studies [77]. We also stress the importance of independently measuring surface charge and $\chi_{\text{DL}}^{(2)}(\omega)$ to fully exploit the exciting perspectives offered by SFG and SHG spectroscopies in interface science. This is nowadays possible thanks to emerging techniques, such as the experimental scheme recently introduced by Liu and coworkers for in situ SFG spectroscopy of oxide surfaces in liquid water [4,78].

We believe that combining SFG and SHG probes of DL water with these approaches, along with advanced theoretical molecular-level 3D EDL models [77], will pave the way for a deeper understanding of the complex relationships between surface topology, interfacial water networks, ion distributions, and electric fields at solid-liquid interfaces.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [79].

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